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TITLE: SOFT HIGHLY ABSORBENT PAPER PRODUCT CONTAINING KETENE DIMER SIZING AGENTS

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SOFT HIGHLY ABSORBENT PAPER PRODUCT CONTAINING KETENE DIMER SIZING AGENTS

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BACKGROUND OF THE INVENTION

The use of ketene dimer based agents in the paper industry to impart sizing, or water resistivity, to paper products is well known. Such agents are commercially available from Hercules Inc. Wilmington, Delaware under trade names such as AQUAPEL® and HERCON®. Some patents disclosing the compositions, variations and uses of these types of agents are:

Inventor	Patent No.	Issued
Aldrich et al.	3,922,243	November 25, 1975
Anderson	3,957,574	May 18, 1976
Aldrich, et al.	3,990,939	November 9, 1976
Aldrich	4,017,431	April 12, 1977
Aldrich et al.	4,087,395	May 2, 1978
Dumas	4,240,935	December 23, 1980
Dumas	4,243,481	January 6, 1981
Dumas	4,279,794	July 21, 1981
Dumas	4,295,931	October 20, 1981
Bankert et al.	4,407,994	October 4, 1983
Bankert et al.	4,478,682	October 23, 1984
Edwards et al.	4,861,376	August 29, 1989
Cenisio et al.	4,919,724	April 24, 1990
Walkden	4,927,496	May 22, 1990
Nolan et al.	5,484,952	January 16, 1996
Zhang	5,525,738	June 11, 1996

The disclosures of which are incorporated herein by reference.

These sizing agents when added to the wet end of the paper machine, at the size press, or to the finished product in an off-machine application impart water resistivity to the paper, by decreasing the hydrophilicity of the sheet. The use of these sizing agents in writing paper, liner board, grocery bag and milk carton is well known, as all of these paper products require sizing.

These types of sizing agents are known to produce very hard sized (high resistivity to wetting) material such a milk carton. The use of these sizing agents in tissue and towel, although not unknown, has been very

limited, because water resistivity is not desirable in these products. To the contrary, it has generally long been a goal in the tissue and towel industry to increase rather than decrease the rate at which the product is wetted and the total amount of water that the product can absorb. An example, however, of the use of ketene dimer sizing agents in tissue and towel products to increase water resistivity is found in European Patent Application No. 0 144 658 in the name of Dan Endres, assigned to Kimberly-Clark Corp.

It has been discovered that the use of ketene dimer sizing agents in tissue and towel increases the softness of these products and that wetting agents or surfactants can be used in conjunction with these sizing agents to eliminate sizing without eliminating the softness benefit. Thus, softness can be increased while not materially effecting the products' water absorbtivity or hydrophilicity.

SUMMARY OF THE INVENTION

In an embodiment of the present invention, a soft highly absorbent tissue product comprising long and short paper making fibers and a ketene dimer sizing agent is provided. A soft absorbent paper product comprising paper making fibers and at least about 1 pound per ton of a ketene dimer sizing agent, the tissue having an absorbency rate test of less than about 40 seconds is further provided.

In an additional embodiment of this invention, a soft absorbent tissue sheet comprising: a first layer and a second layer with the first layer comprising predominately long paper making fibers and the second layer comprising predominantly short paper making fibers and at least one of the layers further comprising a ketene dimer sizing agent and a surface active agent and the layer comprising the ketene dimer being readily wetable by water. This tissue sheet may be creped or through-dried. This soft tissue sheet may have an absorbency rate test less than about 10 seconds.

In yet a further embodiment of the present invention, an absorbent paper sheet having improved softness comprising a first sheet surface and a second sheet surface and a layer comprising paper making fibers. The

layer having a surface which corresponds to a surface of the paper sheet. The surface of the layer having a ketene dimer sizing agent therein and the surface of the sheet having a surface active agent therein. The wetability of the sheet being equivalent to a sheet of similar composition but not having the ketene dimer sizing agent and wetting agent therein. This paper sheet may be a bath tissue that may have a second layer comprising paper making fibers. This paper sheet may be a towel product that may have a second layer comprising paper making fibers. This paper sheet may be a facial tissue that may have a second layer comprising paper making fibers. In a further embodiment the sheet has a third layer.

In still another embodiment, there is provided an absorbent paper sheet having improved softness comprising cellulose paper making fibers and a ketene dimer sizing agent and a wetting agent. The sizing of the sheet being no greater than about three times the sizing of a sheet of similar composition but not having the ketene dimer sizing agent and wetting agent.

In an alternative embodiment of the invention, there is provided a method of making a soft absorbent paper sheet product having improved softness comprising forming an aqueous slurry comprising paper making fibers in a pulper; combining a ketene dimer sizing agent with the paper making fibers; combining a surface active agent with the paper making fibers; and, removing the water from the aqueous slurry to form a paper sheet. The ketene dimer sizing agent may be combined with the paper making fibers prior to, during or after the removal of water from the slurry.

In yet a further alternative embodiment of the invention a soft highly absorbent paper product comprising a blended base sheet having a ketene dimer sizing agent is provided. This blended base sheet may have a blend of long and short paper making fibers

DRAWINGS

Figure 1 is a schematic process flow diagram generally showing the manufacture of paper products.

DETAILED DESCRIPTION OF PRESENTLY PREFERRED EMBODIMENTS OF THE INVENTION

Ketene dimers used in the paper industry to impart sizing, or water resistivity to paper, have a general chemical structure of

$$\begin{array}{l} R_1\text{-CH=C-CH-}R_2 \\ \qquad\quad\;\; |\;\;\; | \\ \qquad\quad\;\; \text{O-C=O} \end{array}$$

in which R_1 and R_2 can be a wide range of carbon backboned structures. Known structures and methods for making these products are disclosed in the aforementioned patents, which were incorporated herein by reference.

When such a sizing agent is used to impart water resistivity to paper, it is theorized that the four-member ring consisting of one oxygen and three carbon atoms, also known as a lactone ring, is primarily responsible for forming a covalent bond to the cellulose fiber. It is theorized that the lactone ring undergoes a reaction with the hydroxyl group on the cellulose. Once this reaction is complete the R groups are then reoriented, through the application of heat, airflow or pressure, away from the cellulose fiber. Thus, they in effect create a hydrophobic mono-molecular layer on the outer surface of the cellulose fiber. It is theorized that this outer hydrophobic surface layer provides the water resistivity to the paper product that is observed when these sizing agents are used.

To countermand this sizing effect, surface active agents such as wetting agents or surfactants can be added to the sheet either in the wet end, to the embryonic web, to the dried sheet or off-machine. Such surface active agents are well known to the art and would include but are not limited to alkoxylated (EO, PO, or BO) alcohols, phenols, polyols, fatty amines, phosphate esters, sorbitan ester, alkoxylated or hydroxylated alkyl polysaccharide, phosolipids, heterocylic compounds, and saturated or unsaturated fatty esters. This list would also include anionic, cationic,

nonionic and amphoteric surfactants, such agents may also be found in or function as defoamers or lubricants. Thus, the softness benefits of the ketene dimer sizing agents are obtained without any material loss of hydrophilicity.

Referring to Figure 1, which is a schematic process flow diagram of a paper making process, cellulose fibers are prepared in a pulper (not shown) to form an aqueous slurry of fibers and water, which is referred to as stock or a stock solution. The stock is pumped into a chest 1, which may be referred to as a dump chest. From the dump chest the stock is pumped to another holding chest 2, which may be referred to as a machine chest. From the machine chest the stock is pumped by the fan pump 3 to the head box 4 of the paper making machine 5. At or before the fan pump, the stock is diluted with water. Usually, and preferably, the dilution is done with return water, referred to as white water, from the paper making machine. The flow of the white water is shown by lines 6 and 7. Prior to dilution the stock is referred to as thick stock, and after dilution the stock is referred to as thin stock.

The thin stock is then dewatered by the forming section 8 of the paper machine to form an embryonic web of wet cellulose fibers. The wet web is than transferred to a dryer 9, which removes water from the wet web forming a paper sheet. The paper sheet then leaves the dryer and is wound on reel 10.

It is to be understood that Figure 1 is a general description of the paper making process and is meant to illustrate that process and is in no way meant to limit or narrow the scope of the present invention. Many variations in this process and equipment are know to those skilled in the art of paper making. For example, various types of dryers can be used including through-air-dryers, Yankee dryers with and without creping, tunnel dryers, and can dryers or any combination of these. Although the schematic generally shows a twin wire type forming section, other forming sections known to the art may be used. Additional components may also be added or removed from the process. For example, screens, filters and refiners, which are not illustrated, may be typically placed between the pulper and the head box. The transfer section 11 of the paper machine may not be present or may be

expanded to include additional water removal devices. Additional steps may also be added on-machine after the dryer and before the reel, such as calendering and the use of a size press, although additional drying is usually required after a size press application is used. Calendering and coating operations may also be conducted off-machine.

Paper sheets can be made of long paper making fibers (softwood), short paper making fibers (hardwood), secondary fibers, other natural fibers, synthetic fibers, or any combination of these or other fibers known to those skilled in the art of paper making to be useful in making paper. Long paper making fibers are generally understood to have a length of about 2 mm or greater. Especially suitable hardwood fibers include eucalyptus and maple fibers. As used herein, the term paper making fibers refers to any and all of the above.

As used herein, and unless specified otherwise, the term sheet refers generally to any type of paper sheet, e.g., tissue, towel facial, bath or a heavier basis weight product, creped or uncreped, blended, multilayer or single layered, and multiplied or singleplied.

The ketene dimer sizing agent can be added in the wet end of the paper machine to either the thick or thin stock as is well known in the art. In addition to wet end addition, the ketene dimer sizing agent can be added to the embryonic web, partially dried sheet or dried sheet. It can be sprayed on or applied by roll application either as an on- or off-machine application. The optimum application point and method will depend on the particular paper type and machine, however, they should be selected to optimize the distribution of the agent in or on the sheet, minimize the effect on the runability of the machine, such as to reduce the amount of foam, and maximize the amount of softness increase for quantity of agent used. The wetting agent should preferably be applied downstream of the addition point of the sizing agent. However, particularly in wet end applications, the wetting agent may be added at any point with respect to the sizing agent point of addition. It is, however, optimal to have the addition points of the sizing agent and surface action agent as close as possible.

The ketene dimer sizing agent can be derived from either plant or animal fatty acids, which can have branched or unbranched, saturated or unsaturated R groups. Moreover, at least one R group may be substituted with an H. The presently preferred R groups range from C_1 - C_{29}, it is further desirable that the chain lengths for these R groups ranges from around C_6 to around C_{22} and still further desirable that the chain length range from around C_8 - C_{18}. Additionally, it is presently believed that it is easier to mask the sizing affect of chain lengths in the range from around C_8 to C_{12}.

The amount of ketene dimer sizing agent that is added to the paper will depend on the ketene dimer being used, type and composition of the paper being made, and the manner and point in the paper making process in which the agent is added. Presently between about 0.25 to about 5 pounds per ton of paper (dry basis weight) of sizing agent may be used, although depending on the application the benefits of this invention may be seen with lower and higher amounts. From about 0.5 to about 4 pounds per ton may optimally be used for wet end addition. The practical upper limits for the amount of sizing agent used will principally be controlled by machine runability, water absorbtivity of the sheet, and cost. The amount of wetting agent or surfactant used will depend on the type of agent and the amount of sizing agent used. Sufficient amounts of wetting agent to mask the sizing must be used.

The addition of the wetting agent to the sheet prevents the sizing agent from materially effecting the wetability of the sheet, i.e., the sheet is not sized. Thus, the rate of water absorption and the total amount of water that a sheet softened with a ketene dimer sizing agent and wetting agent can absorb is not materially different from an equivalent sheet that does not have those agents. These sheets can have as much a one to two fold increase in sizing compared to a sheet without the sizing agent, and still exhibit sufficient hydropholicity.

Wetability of the sheet, or the amount of sizing, can be measured by a number of ways. Of course, all samples should be aged and tested in accordance with TAPPI standards.

Absorbency Rate Test - The absorbency rate is the time it takes for a product to be thoroughly saturated in distilled water. Samples are prepared as 2½ inch squares composed of 20 finished product sheets using a die press (e.g. TMI DGD from Testing Machines Incorporated Inc., Amityville, N.Y. 11701). The ply of a finished product dictates the number of individual sheets:

1-ply:	20 individual sheets
2-ply:	40 individual sheets
3-ply:	60 individual sheets

When testing soft rolls (single ply of tissue coming off the tissue machine before plying at the rewinder), 40 individual softroll sheets are used per sample.

The samples are stapled in all four corners using Swingline S.F. 4 speedpoint staples (the staples are 1/2-inch wide with 1/4-inch long legs). Samples are tested in a constant temperature water bath at a depth of at least 4 inches (maintained through out testing) maintaining distilled water at 30 +/- 1° Celsius. The sample is held close to the water surface (staple points in the down position) and then dropped flat on the water surface. A stopwatch (readable to 0.1 s) is started when the sample hits the water. When the sample is completely saturated; the stopwatch is stopped and the absorbent rate is recorded. A minimum of five samples are tested.

All tests were conducted in a standard laboratory atmosphere of 23+/1 1° Celsius and 50 +/- 2% RH. All samples were stored in this laboratory for at least 4 hours before testing. All samples are aged and tested at TAPPI conditions.

Hercules Size Test (HST) – A small volume of ink is placed on the paper sample to be tested. The sample amount is typically 1 to 5 layers of paper. A photo electric eye then measures the time that is required for the reflectance of the sample to drop to a specific level from its original point. This test is typically used for bleached board, cup stock, fine paper and

linerboard grades. This test may be used for measurement of sizing in facial tissue grades.

Flotation Tests – A sample of paper is floated on a aqueous solution. The test is timed and reaches completion when the sample has become completely saturated with the test solution. The type of solution use is dependent on the end use of the paper. Typical solutions used are ink, water, fluorescent dye, and ammonium solutions The use of flotation tests are usually limited to fine paper grades. Linerboard, gypsum board, and cup stock are typically not tested with this method due to the excessive time required to saturate the sample. A water bath saturation test may be used for measurement of sizing in facial tissue grades.

Boiling Boat – This test measures the time requirement for 'boat' shaped paper sample to completely saturate in boiling water. This test is typically used for highly sized grades such as gypsum and linerboard.

Valley Size Test – A sample of paper is connected at each end by an electrode. The sample is immersed into a water solution and the conductivity of the paper sample, after a predetermined period of time, is measured. The use of this test is typically limited to cylinerboard paper grades.

Currier – Sizing is measured by the time necessary for a paper sample, soaking in a aqueous fluid, to complete an electrical circuit. This test has been very popular for use in linerboard grades.

Immersion Test – A paper sample is weighted and then soaked in a water bath for a predetermined period of time. Sizing is measured by the weight of water that has been absorbed during the test. This test is often used for fine paper grades.

Edgewick – A sample of paper is immersed, on its edge, into a liquid sample of lactic acid, peroxide, coffee, etc. This test measures the amount of liquid that is picked up by the paper over a defined period of time. This test is exclusively used for food packaging grades such as milk cartons and other liquid for packaging applications.

Klemm – The end of a paper sample is immersed into a bath of liquid. Sizing is measured by the amount of time it takes for the liquid to raise up the sample to a predetermined point. This test is very flexible and can be used for many sized grades.

Typically, tissue made without the use of sizing agents shows an absorbency rate test of from about 1 second to about 10 seconds or slightly less. Towel made without sizing agents will typically show an absorbency rate of about 1 to about 50 seconds. When tissue and towel are sized with a ketene dimer sizing agent it can be anticipated that sizing levels, or water resistivity, will substantially increase. For example, absorbency rate tests for tissue can increase as much as 25 seconds or more. Tissue having improved softness from the use of ketene dimer sizing agents in conjunction with surface active agents remain hydrophilic, having a very low resistance to wetting, i.e., they are not sized and thus wet easily. The water absorbency rate test for such softened sheets are from around 1 to around 4 seconds, but may be up to about 10 seconds or more depending on the type of paper, basis weight and other physical characteristics of the sheet. For tissue and towel products water absorbency test results of less than 40 seconds are believed to show that the sheet is still substantially hydrophilic, and are viewed as low or negligible levels of sizing.

Sizing agents may exhibit a threshold effect in the development of water sensitivity. Thus, for example, the initial ¼ to 2 pounds of sizing agent per ton of paper may develop little or no increased water resistivity. At any higher amounts the increase in water resistivity may be substantial. This threshold level will, of course, vary from sheet to sheet and process to process. The use of surface active agents in conjunction with sizing agents permits the addition of sizing agent above the threshold amount to obtain the softness benefits without experiencing a dramatic loss in hydrophilicity.

Following are examples of how ketene dimer sizing agents in conjunction with surface active agents can be used to increase softness while having no applicable effect on hydrophilicity.

Handsheets studies are blended basesheets containing 50% hardwood and 50% softwood dosed with 1 pound per ton of a ketene dimer sizing agent and 1 pound per ton PEG 400 dioleate (ethoxylated fatty alcohol). This would provide good softness and better water absorbency than 1 pound per ton of sizing agent alone.

Handsheets studies are blended basesheets containing 70% hardwood and 30% softwood dosed with 1 pound per ton of a ketene dimer sizing agent and 1 pound per ton hydroxylated lecithin (phosolipid) to give good softness and better absorbency rates than handsheets with 1 pound per ton of a ketene dimer sizing agent alone.

Handsheets studies are blended basesheets containing 70% hardwood and 30% softwood dosed with 2 pound per ton of a ketene dimer sizing agent and 1 pound per ton Trycol 6974 (POE (10) nonylphenol) to give better absorbency rates than handsheets with 2 pound per ton of a ketene dimer sizing agent alone.